Lecture 10:
Solid-State Electrochemistry II
Kinetics of Electrode Reactions
Butler-Volmer Equation/Frumkin Correction

Prof. Qiyang Lu
Solid State Ionics (SSI) Laboratory
School of Engineering, Westlake University

西湖大學
WESTLAKE UNIVERSITY

Fall 2023 MSE 5007
Solid State Ionics

SSI Lab
WESTLAKE UNIVERSITY

Things we will discuss in this lecture

Kinetics of Electrode Reactions:

- How to build a model for charge transfer at electrode surfaces?
- What are the key assumptions for Butler-Volmer equations?
- What does the η-I curve look like at small/large overpotentials?

Frumkin Correction:

- What is the Frumkin Effect? How does the space charge layer affect the kinetics at electrode surfaces/interfaces?

Goal of this lecture: you should be able to answer the questions above now (hopefully) :)

The importance of electrode kinetics

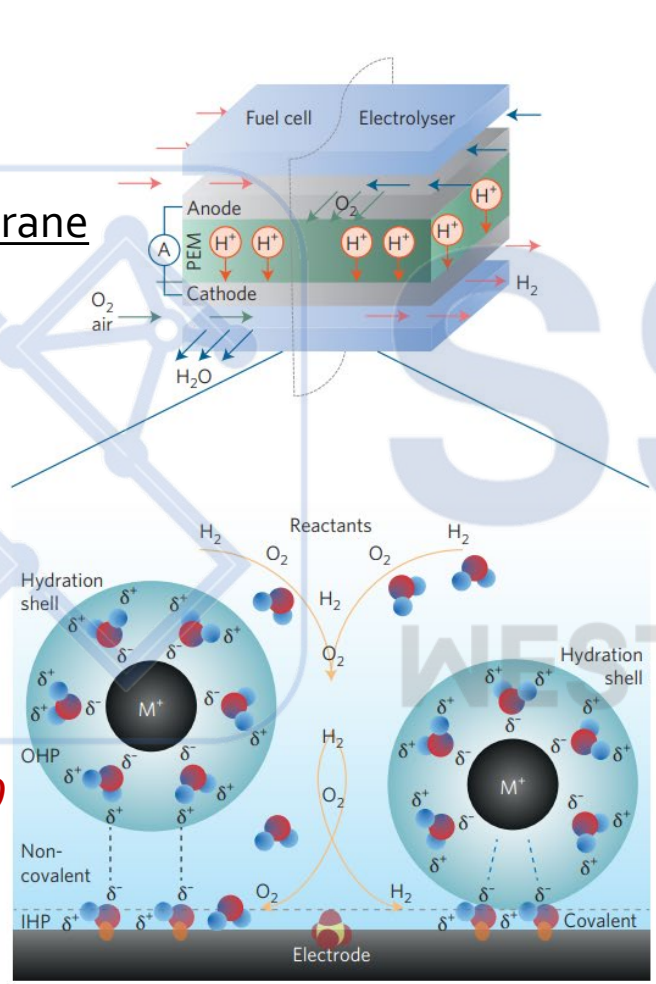
Proton-**E**xchange **M**embrane **F**uel **C**ell (**PEMFC**)

Aqueous solution system

Oxygen ***R***eduction ***R***eaction (***ORR***)

$4H^+ + O_2 + 4e^- \rightarrow 2H_2O$

Electrocatalysis happens at ***interfaces***!

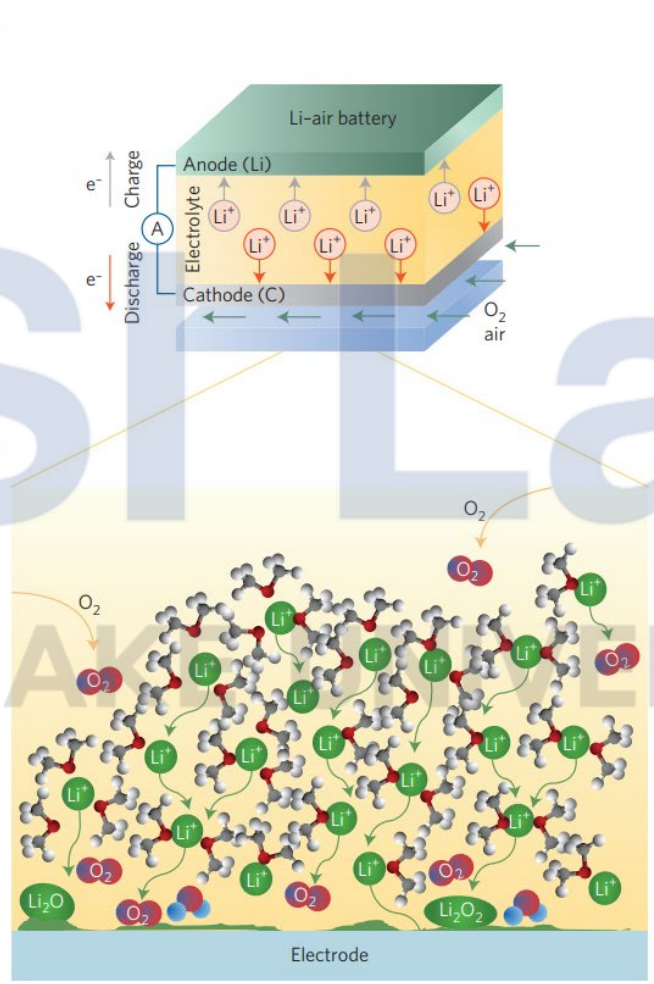


Stamenkovic, Markovic et al., *Nat. Mater.*, **16**, 57–69 (2017)

Lithium-Air Battery

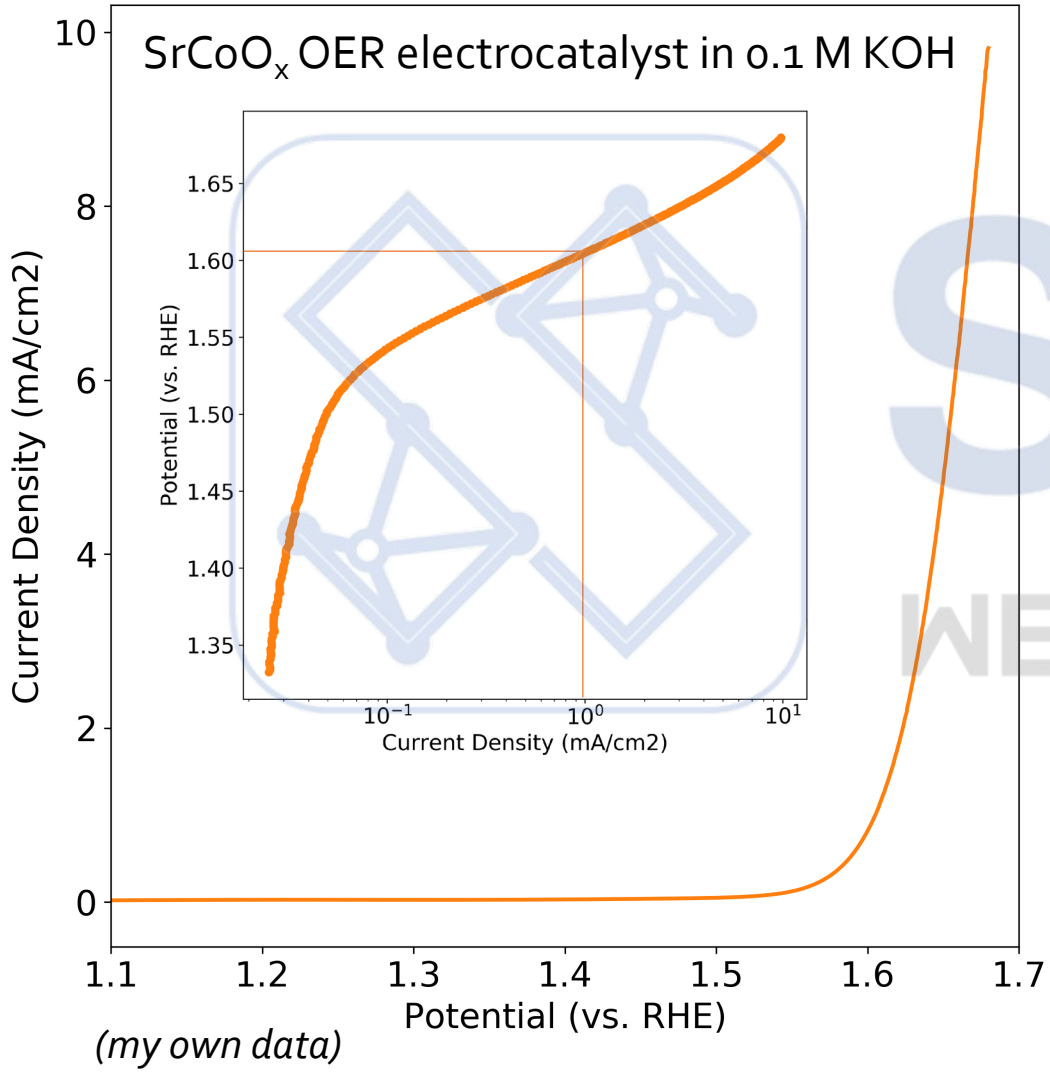
Organic solution system

$2Li^+ + O_2 + 2e^- \rightarrow Li_2O_2$

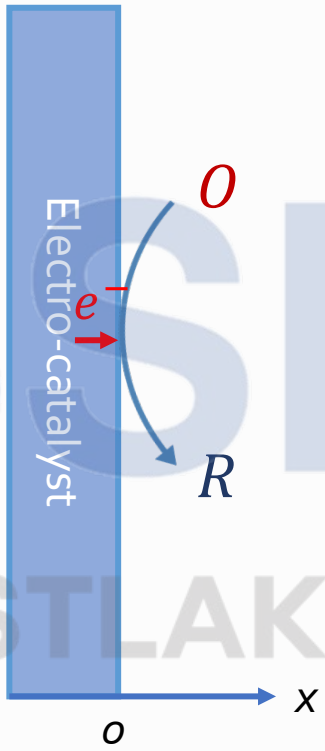


In either case, ***electro-catalytic*** reaction determines the performance of cells

How to understand the *I-E* characteristics?



(my own data)



$$O + e^- \rightleftharpoons R$$

Equilibrium potential with fixed $[O]_{x=0}$ and $[R]_{x=0}$ (concentrations are only evaluated at interfaces):

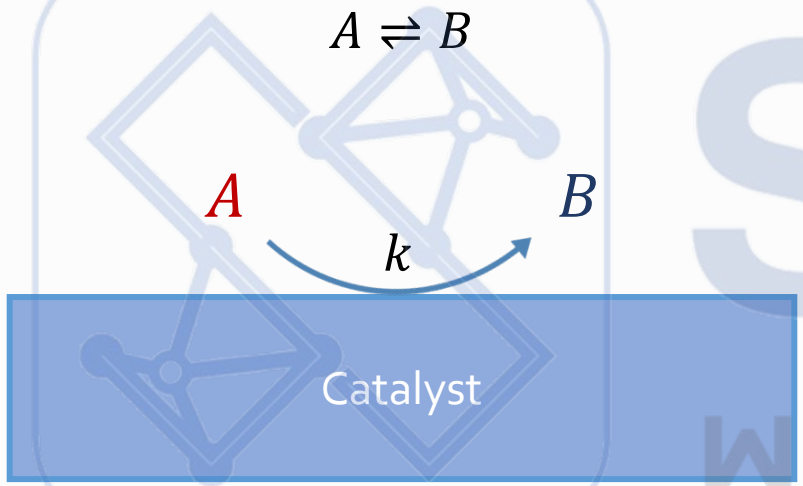
$$E_{eq} = E^{0\prime} + \frac{RT}{F}\ln\left(\frac{[O]_{x=0}}{[R]_{x=0}}\right)$$

Nernst Equation

- The current (I) is directly related to the rate of the electrochemical *rxn* (so-called Faradaic current);
- The potential applied (controlled) E can be far away from E_{eq};
- We seek a theory to make prediction of I-E curves.

The difference between catalysis (chemical) and electro-catalysis (electrochemical)

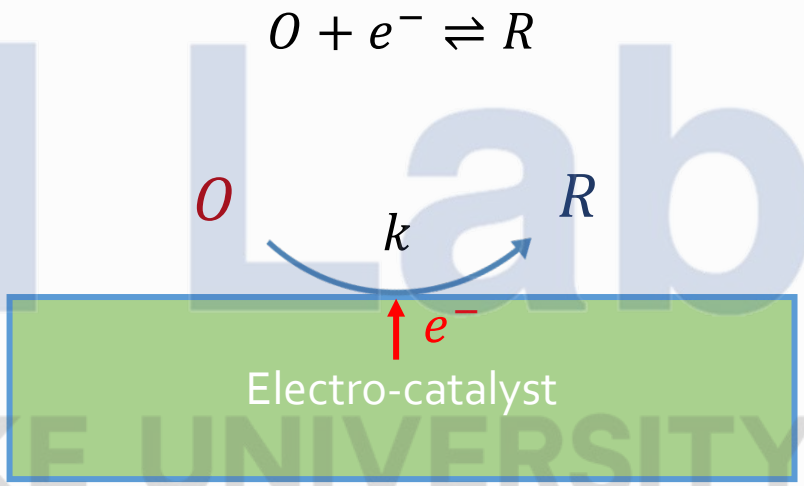
Chemical Reaction (*rxn*)
(Catalysis)



Reaction rate is determined by

- Concentration of reactant and product ($[A]$ and $[B]$)
- Temperature

Electrochemical Reaction
(Electro-catalysis)

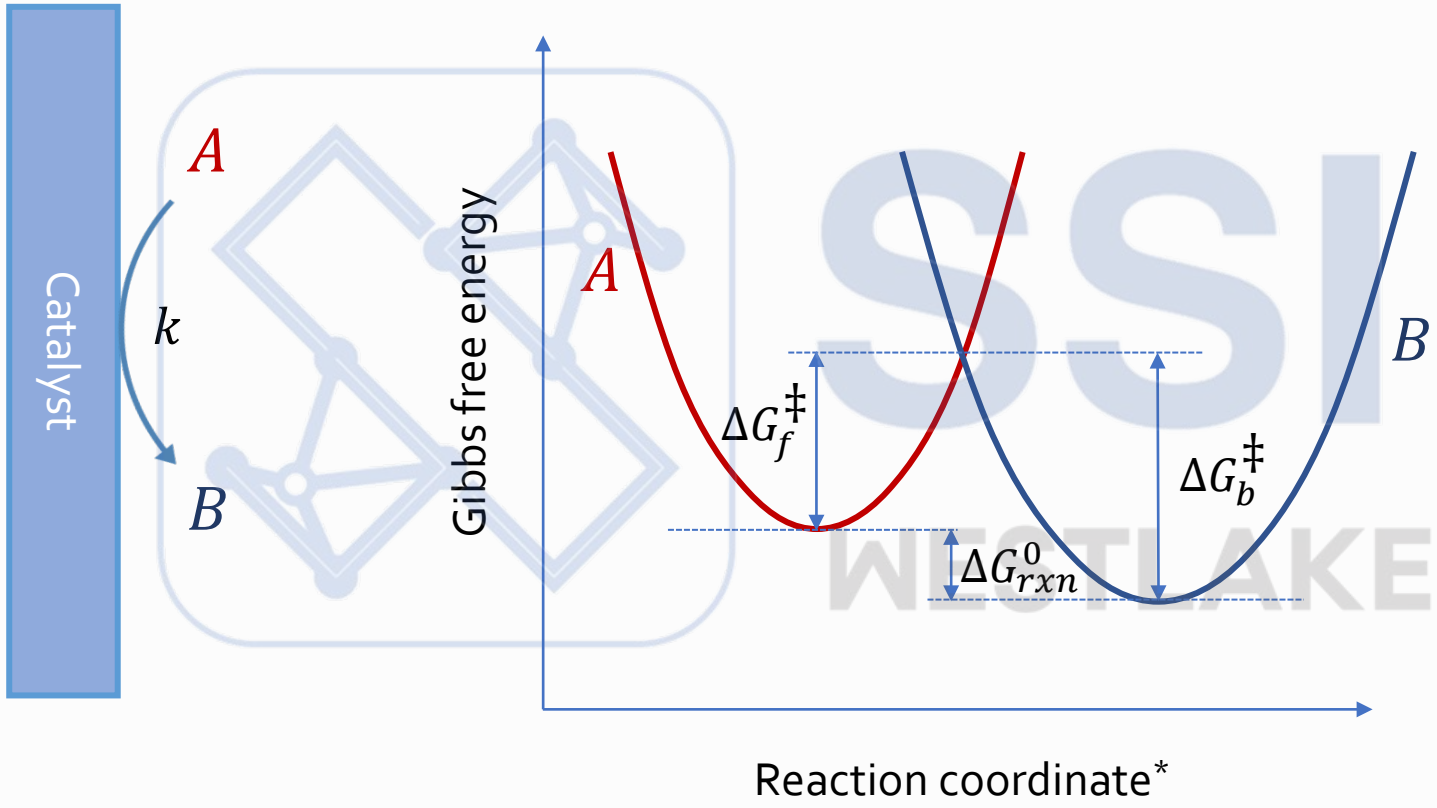


Reaction rate is determined by

- Concentration of reactant and product ($[O]$ and $[R]$)
- Temperature
- Electrode potential (which affects energy of ***electrons***)
- Concentration of electrons (?) → *quantum* effect

Fundamentals on thermal catalysis (chemical reaction)

Transition State Theory



$$A \underset{k_b}{\overset{k_f}{\rightleftharpoons}} B$$

$$k_f = A_f exp(-\Delta G_f^{\ddagger}/RT)$$

$$k_b = A_b exp(-\Delta G_b^{\ddagger}/RT)$$

Prefactor (or **Frequency factor**)

Erying Equation $A = \kappa \frac{k_B T}{h}$

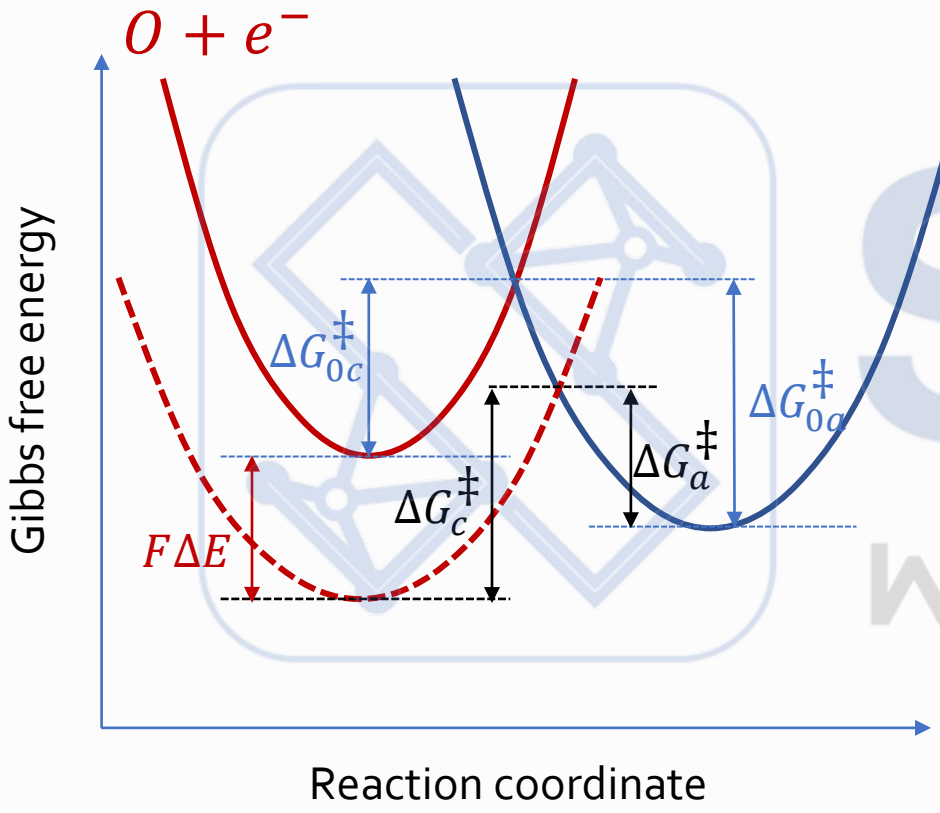
Transmission coefficient $0 < \kappa < 1$

Planck's constant ($h = 4.135 \times 10^{-15} eV/Hz$)

At equilibrium: $k_f[A] = k_b[B]$

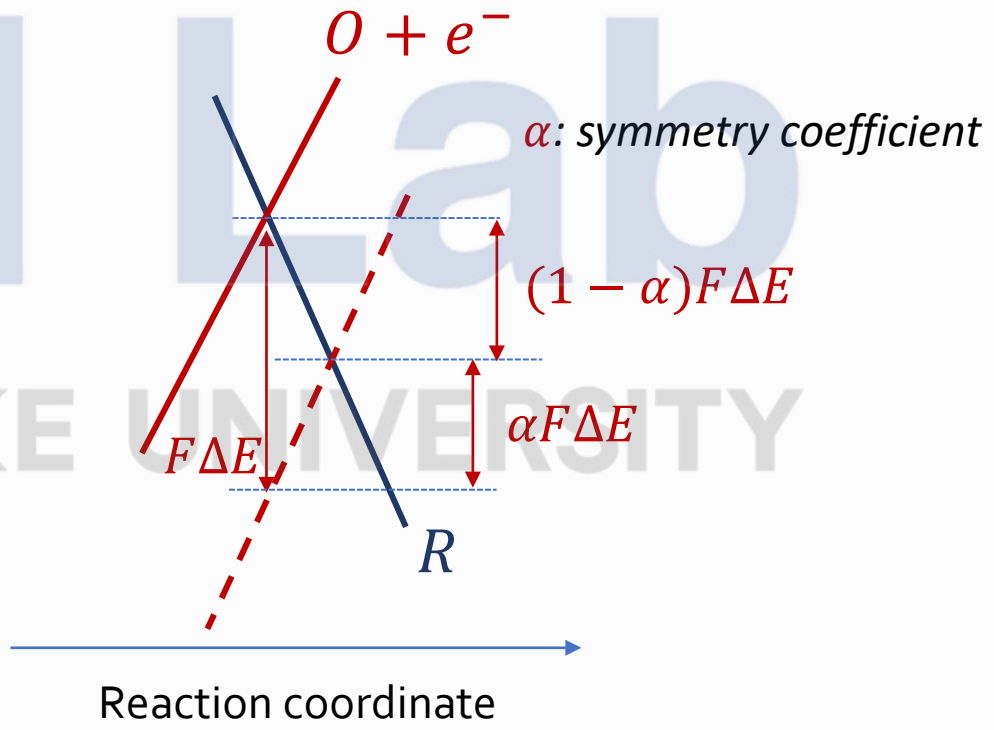
* "an ***abstract*** *one-dimensional coordinate which represents progress along a reaction pathway*" ***-Wikipedia***

Electro-catalysis: charge transfer reaction



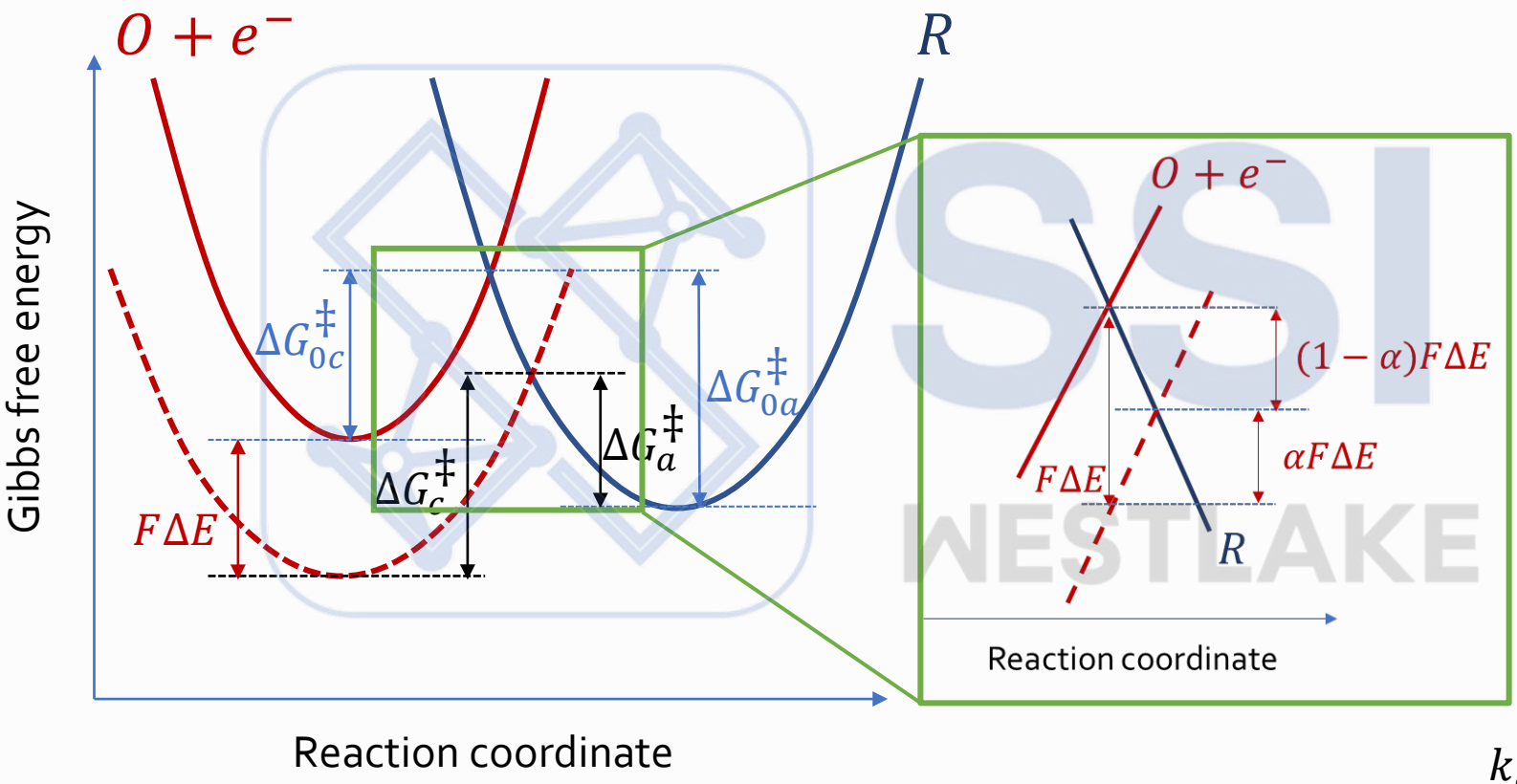
Note: applied electric potential (ΔE) only changes the energy of $O + e^-$ due to the *charge of electrons*

$$O + e^- \underset{k_a}{\overset{k_c}{\rightleftharpoons}} R$$



Question: How does applied electric potential (ΔE) change the free energy of activation ($\Delta G^{\ddagger}$)?

Electro-catalysis: charge transfer reaction



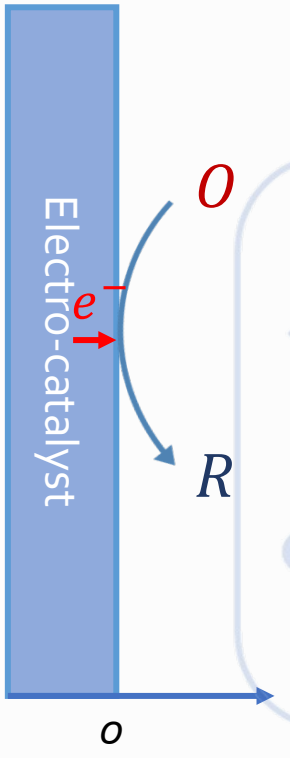
$$O + e^- \underset{k_a}{\overset{k_c}{\rightleftharpoons}} R$$

$$\Delta G_c^{\ddagger} = \Delta G_{0c}^{\ddagger} + \alpha F\Delta E$$
$$\Delta G_a^{\ddagger} = \Delta G_{0a}^{\ddagger} - (1-\alpha)F\Delta E$$

$$k_c = A_c exp\left(-\Delta G_c^{\ddagger}/RT\right) = A_c exp\left(-\Delta G_{0c}^{\ddagger}/RT\right) exp(-\alpha F\Delta E/RT)$$

$$k_a = A_a exp\left(-\Delta G_a^{\ddagger}/RT\right) = A_a exp\left(-\Delta G_{0a}^{\ddagger}/RT\right) exp((1-\alpha)F\Delta E/RT)$$

The Butler-Volmer (B-V) equation



$$O + e^- \underset{k_a}{\overset{k_c}{\rightleftharpoons}} R$$

Note that $\Delta E = E - E^{0\prime}$ is the electrochemical driving force for the reaction

$E^{0\prime}$ is so-called *formal potential* $[O]_{x=0} = [R]_{x=0}$

At equilibrium ($E = E^{0\prime}$, which means ΔE is *o*)

$$k^0 = A_a exp\left(-\Delta G_a^{\ddagger}/RT\right) = A_c exp\left(-\Delta G_c^{\ddagger}/RT\right)$$

Standard rate constant k^0

Non-equilibrium

Forward rxn (cathodic)

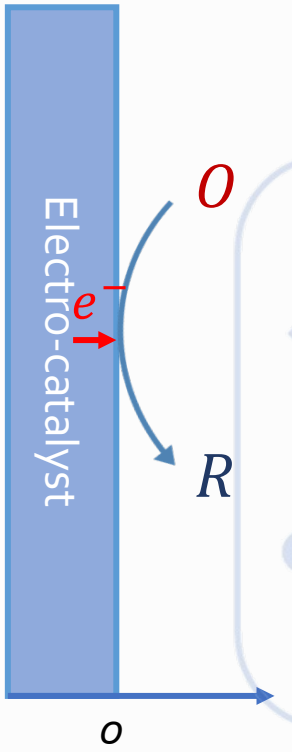
$$\vec{R} = k_c[O]_{x=0} = k^0 exp\left(-\frac{\alpha F \Delta E}{RT}\right)[O]_{x=0}$$

Backward rxn (anodic)

$$\overleftarrow{R} = k_a[R]_{x=0} = k^0 exp\left(\frac{(1-\alpha) F \Delta E}{RT}\right)[R]_{x=0}$$

Note: Electrocatalytic reaction only happens at the interface ($x = 0$); We assume mass transport (diffusion) is fast ($[O]_{x=0} \approx [O]_{x=\infty}$)

The Butler-Volmer (B-V) equation



$$O + e^- \underset{k_a}{\overset{k_c}{\rightleftharpoons}} R$$

Non-equilibrium $\quad I = FA(\vec{R} - \overleftarrow{R}) = FA\,k^0\left[exp\left(-\frac{\alpha F \Delta E}{RT}\right)[O]_{x=0} - exp\left(\frac{(1-\alpha)F\Delta E}{RT}\right)[R]_{x=0}\right]$

Electrode surface area

$$I = FA\,k^0\left[exp\left(-\frac{\alpha F(E-E^{0\prime})}{RT}\right)[O]_{x=0} - exp\left(\frac{(1-\alpha)F(E-E^{0\prime})}{RT}\right)[R]_{x=0}\right]$$

Butler-Volmer Equation

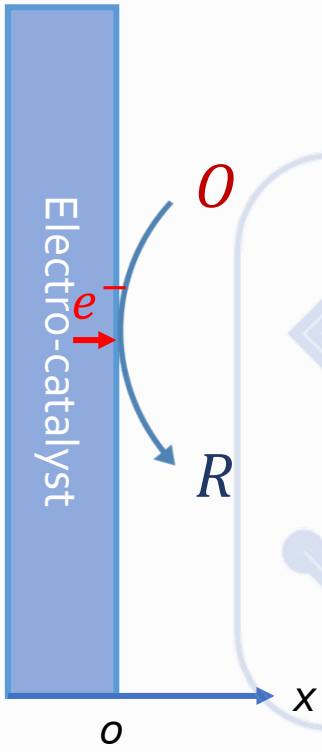
"*Sanity check*": at which potential E, $i = 0$?

$$exp\left(-\frac{\alpha F(E-E^{0\prime})}{RT}\right)[O]_{x=0} = exp\left(\frac{(1-\alpha)F(E-E^{0\prime})}{RT}\right)[R]_{x=0}$$

$$E_{eq} = E^{0\prime} + \frac{RT}{F}\ln\left(\frac{[O]_{x=0}}{[R]_{x=0}}\right)$$

Nernst Equation!

The Butler-Volmer (B-V) equation



$$O + e^- \underset{k_a}{\overset{k_c}{\rightleftharpoons}} R$$

We define *overpotential* as extra driving force compared with E_{eq} *Overpotential* $\eta = E - E_{eq}$

$$I_0 = FA\,k^0([O]_{x=0})^{1-\alpha}([R]_{x=0})^{\alpha}$$ I_0 : *Exchange current*

$$I = FA\,k^0\left[exp\left(-\frac{\alpha F(E-E^{0\prime})}{RT}\right)[O]_{x=0} - exp\left(\frac{(1-\alpha)F(E-E^{0\prime})}{RT}\right)[R]_{x=0}\right]$$

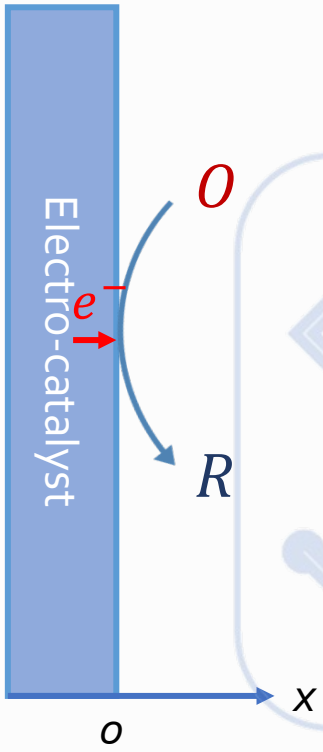
$$I = I_0\left[exp\left(-\frac{\alpha F(E-E_{eq})}{RT}\right) - exp\left(\frac{(1-\alpha)F(E-E_{eq})}{RT}\right)\right]$$
$$= I_0\left[exp\left(-\frac{\alpha F\eta}{RT}\right) - exp\left(\frac{(1-\alpha)F\eta}{RT}\right)\right]$$

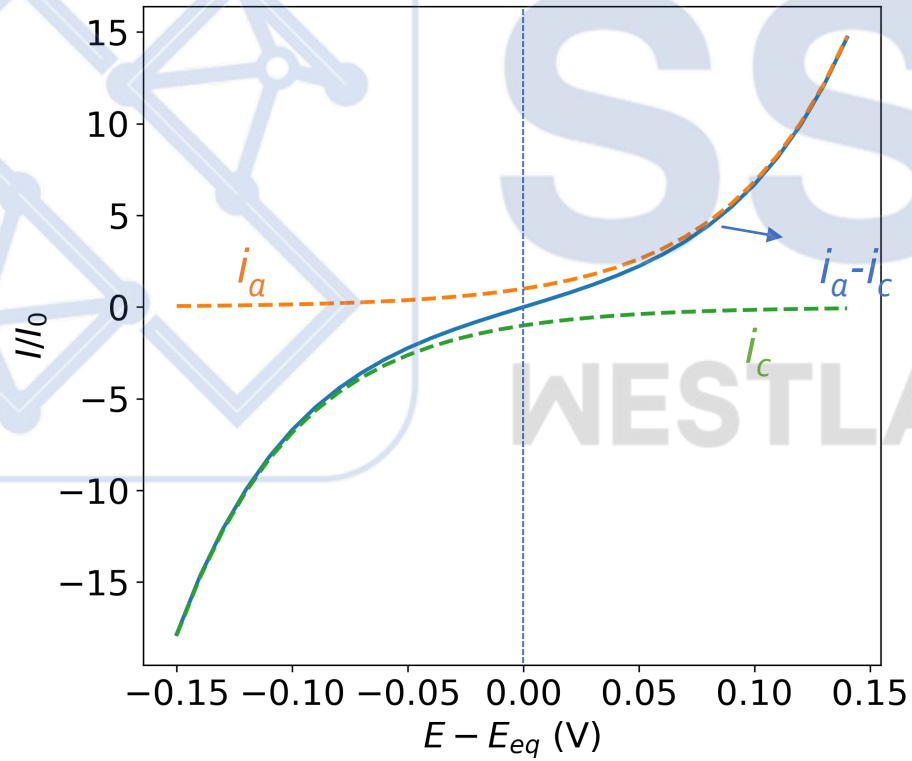
Butler-Volmer Equation
(the most common form)

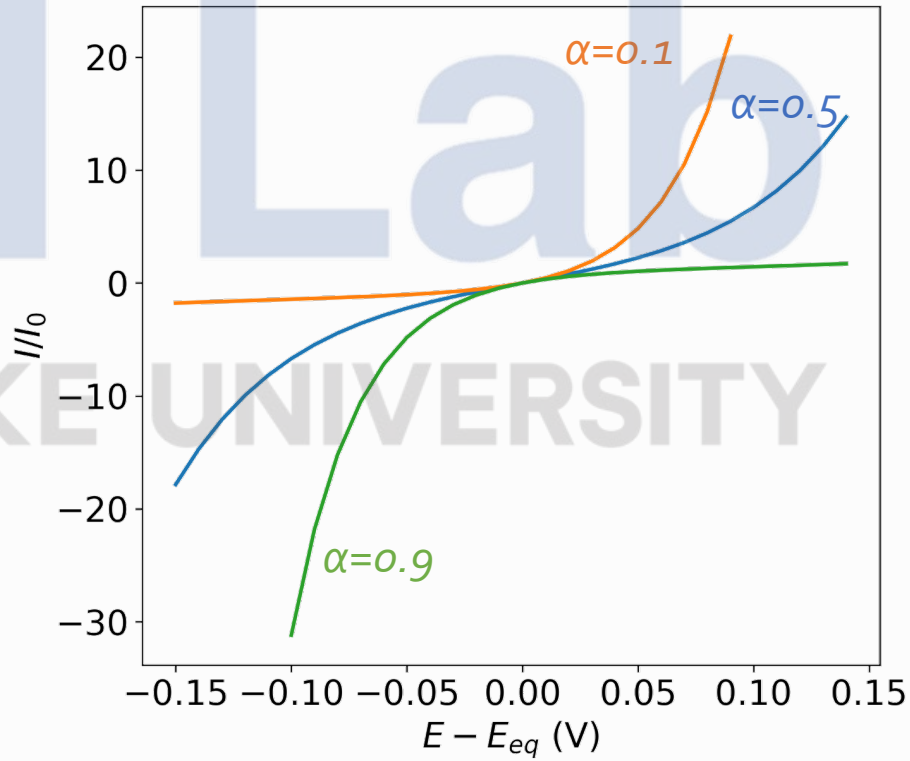
The Butler-Volmer (B-V) equation

$$I = I_0 \left[exp\left(-\frac{\alpha F(E - E_{eq})}{RT} \right) - exp\left(\frac{(1-\alpha) F(E - E_{eq})}{RT} \right) \right]$$

Butler-Volmer Equation
(the most common form)







The Butler-Volmer (B-V) equation: approximations

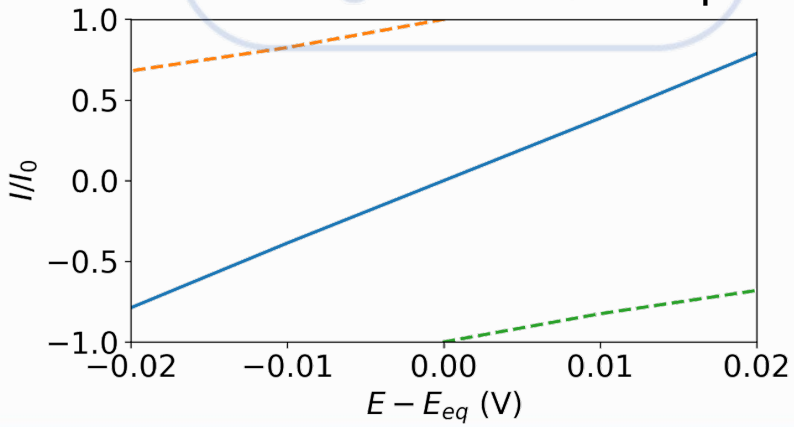
$$I = I_0\left[exp\left(-\frac{\alpha F(E-E_{eq})}{RT}\right) - exp\left(\frac{(1-\alpha)F(E-E_{eq})}{RT}\right)\right]$$

Butler-Volmer Equation

If $E - E_{eq}$ is small ($e^x \sim 1 + x$)

$$I = -\frac{I_0 F}{RT}(E - E_{eq})$$

Charge transfer resistance $R_{ct} = \left|\frac{(E-E_{eq})}{I}\right| = \frac{RT}{I_0 F}$



If $E - E_{eq} \gg 0$ (compared with RT/F)

$$I = -I_0 exp\left(\frac{(1-\alpha)F(E-E_{eq})}{RT}\right)$$

Only ***anodic*** current matters

If $E - E_{eq} \ll 0$ (compared with RT/F)

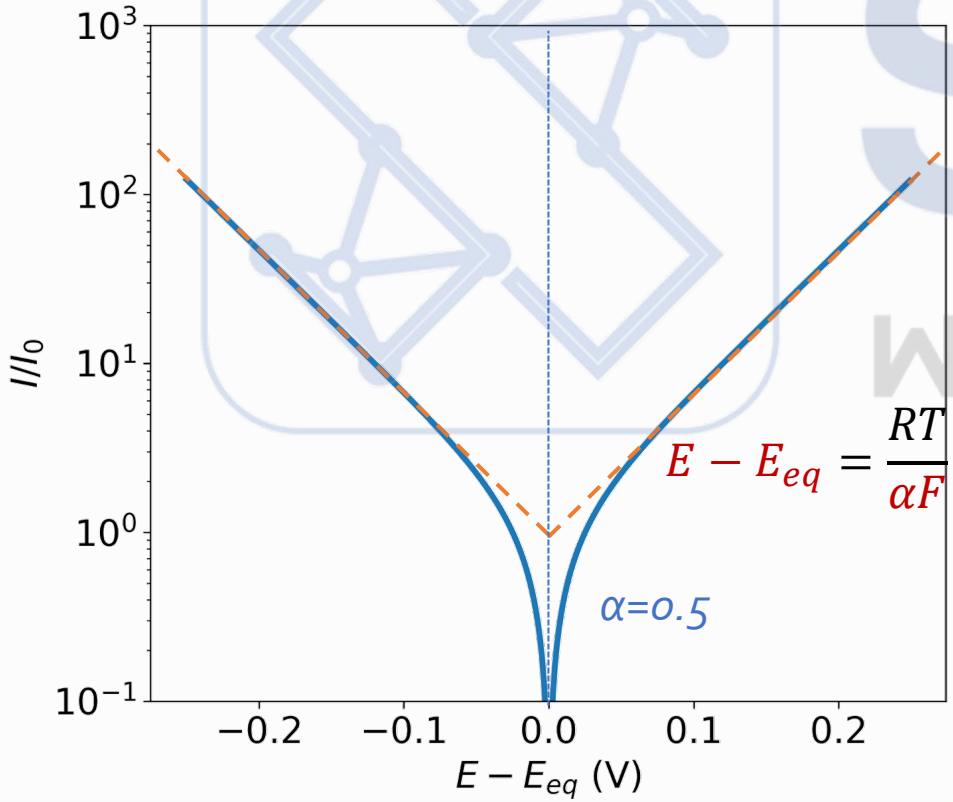
$$I = I_0 exp\left(-\frac{\alpha F(E-E_{eq})}{RT}\right)$$

Only ***cathodic*** current matters

Tafel plot: extract α and I_0

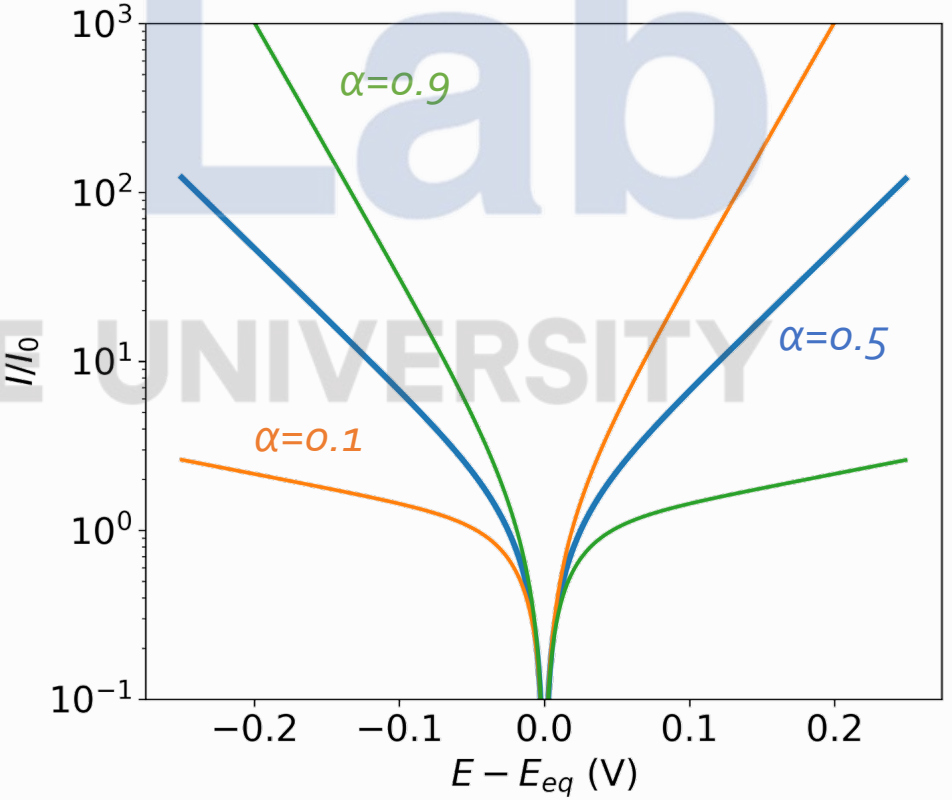
$$I = -I_0 exp\left(\frac{(1-\alpha)F(E-E_{eq})}{RT}\right) \quad (E - E_{eq} \gg 0)$$

$$I = I_0 exp\left(-\frac{\alpha F(E-E_{eq})}{RT}\right) \quad (E - E_{eq} \ll 0)$$



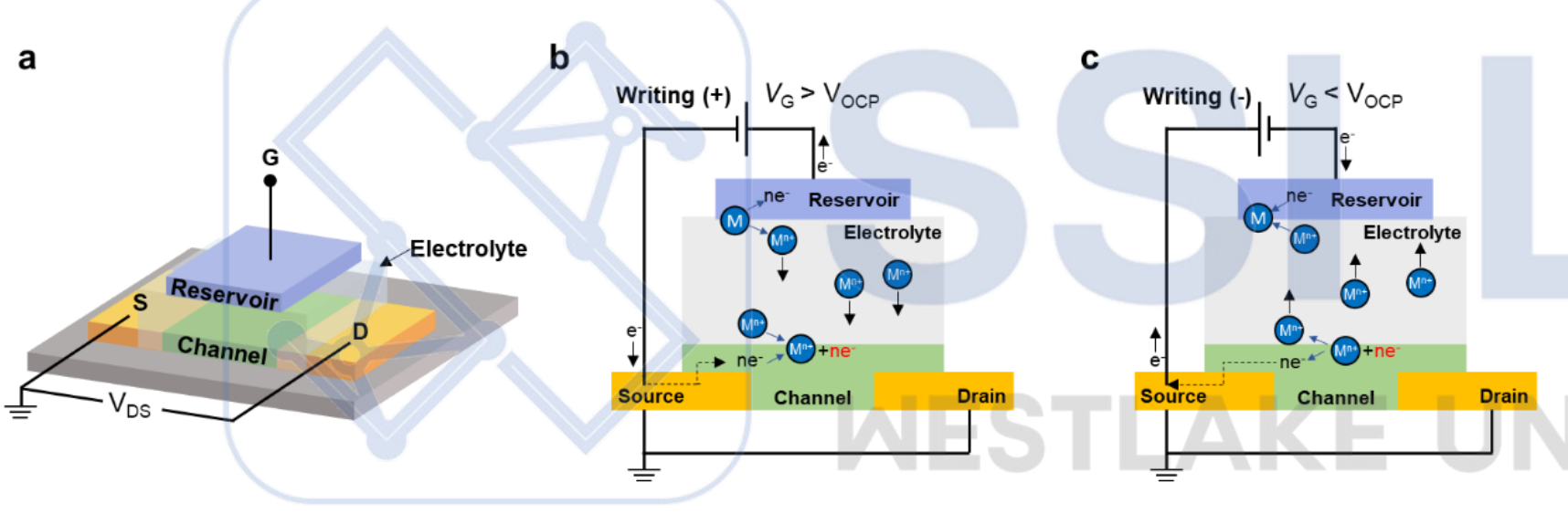
$$E - E_{eq} = \frac{RT}{\alpha F} lnI_0 - \frac{RT}{\alpha F} ln|I|$$

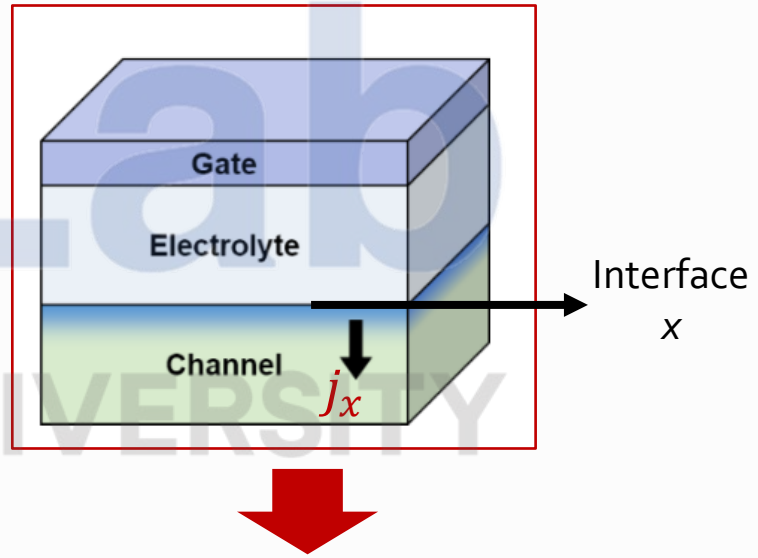
$\alpha \neq 0.5$ → Forward and backward current not symmetric any more



Beyond electrocatalysts: the application of B-V equation

The Butler-Volmer (B-V) equation can be used to describe the kinetics of *charge transfer* at interfaces, not limited to electrocatalysts.

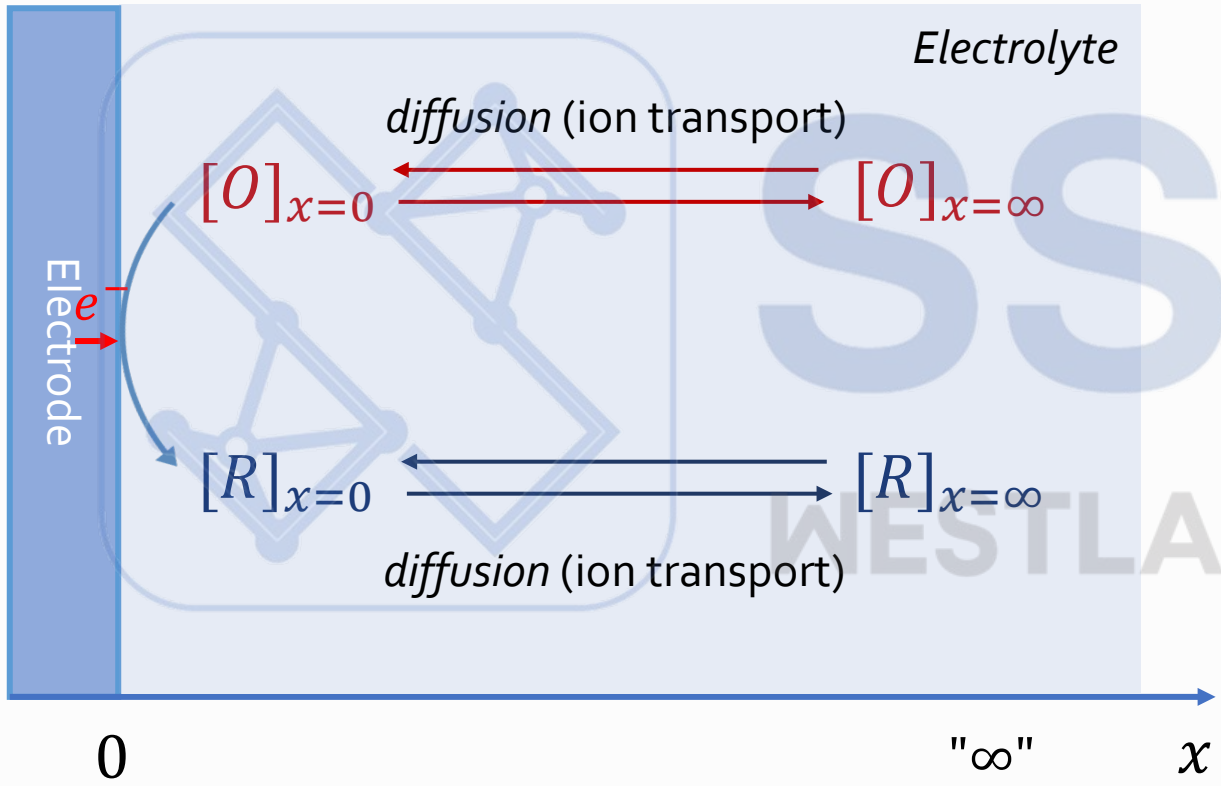




- *Electrochemical Ionic Synapses* use redox rxn to tune the conductivity of the channel material for memory and computing;
- Faradaic current density at interface *x* (electrolyte/channel interfaces) is modeled using B-V.

$$j_x = j_{x_0}\exp\left(\left(\frac{\alpha_x z F V_x}{RT}\right) - \exp\left(-\frac{(1-\alpha_x) z F V_x}{RT}\right)\right)$$

Electrochemical reaction: Nernst equation



$$O + e^- \rightleftharpoons R$$

Equilibrium potential with fixed $[O]_{x=0}$ and $[R]_{x=0}$

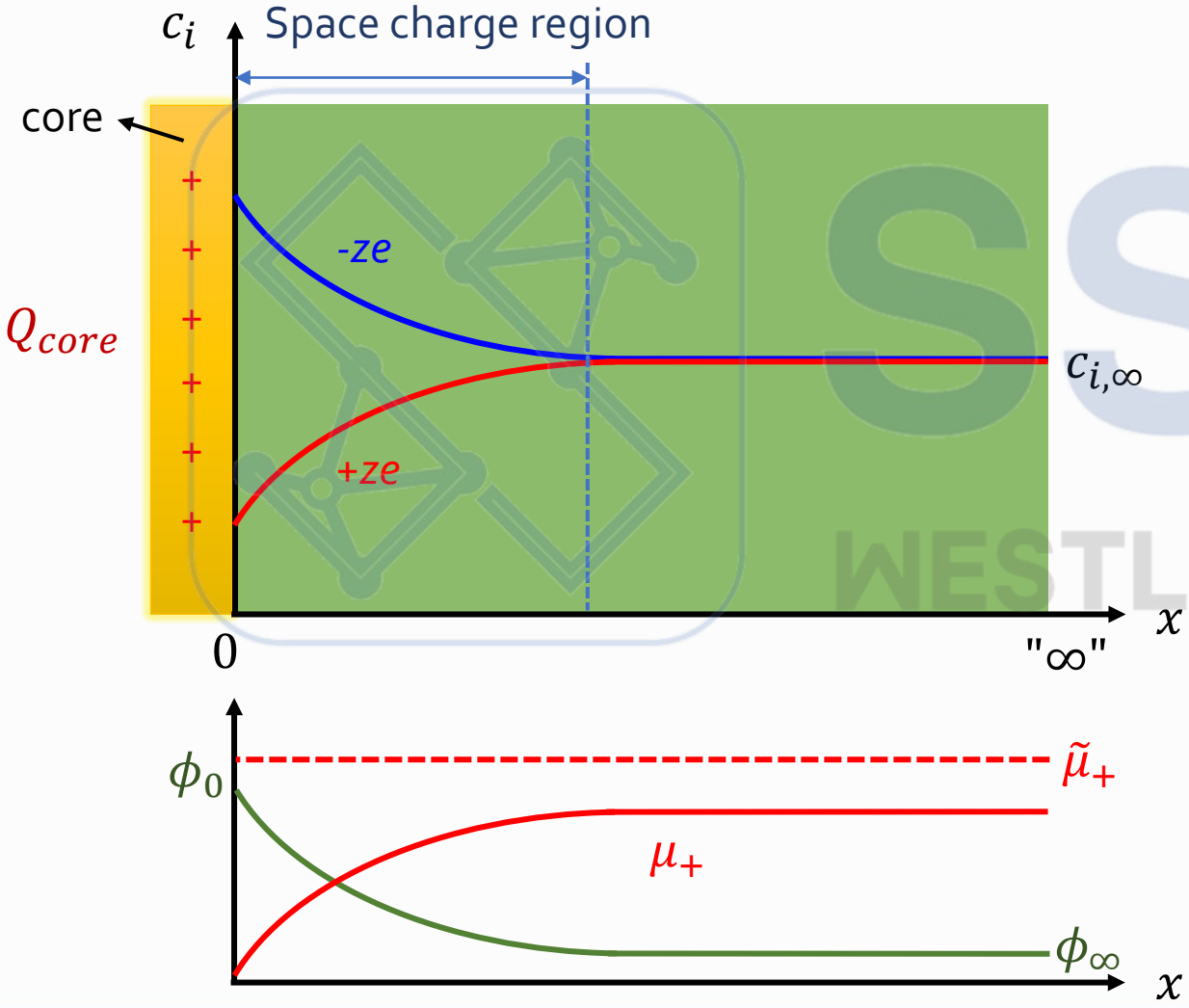
(concentrations are only evaluated *at electrode/electrolyte interfaces*)

Nernst Equation

$$E_{eq} = E^{0\prime} + \frac{RT}{F}\ln\left(\frac{[O]_{x=0}}{[R]_{x=0}}\right) = E^{0\prime} + \frac{RT}{F}\ln\left(\frac{[O]_{x=\infty}}{[R]_{x=\infty}}\right)$$

Fast diffusion

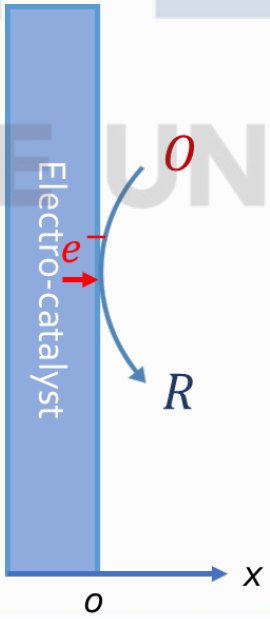
The effect of space charge layer on electrode kinetics



Recall the concentration profile in the space charge layer:

$$c_+(x) = c_{i,\infty}\exp(-\frac{ze\phi(x)}{k_BT})$$

$$c_-(x) = c_{i,\infty}\exp(+\frac{ze\phi(x)}{k_BT})$$



Recall exchange current I_0

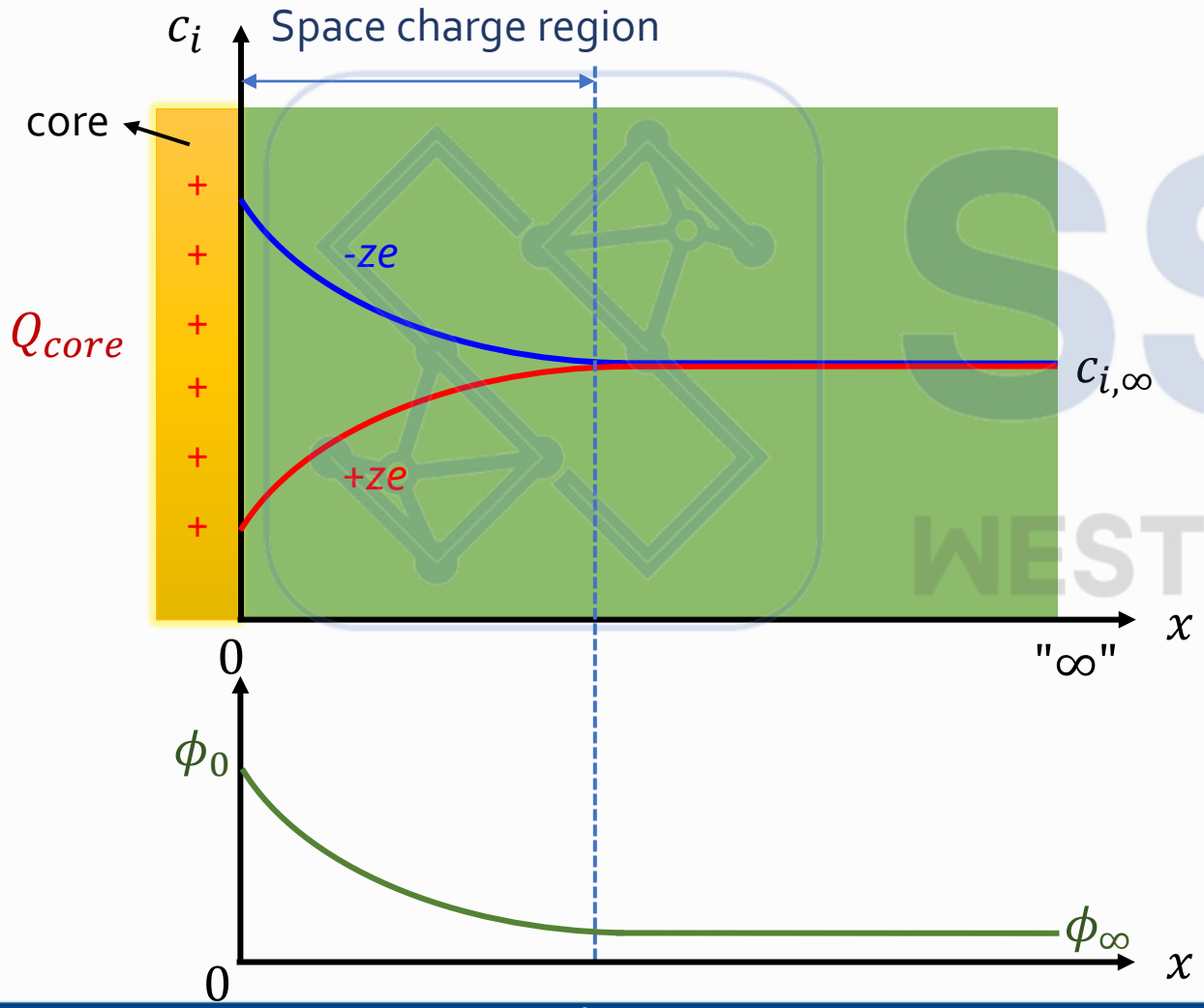
$$I_0 = FA\,k^0([O]_{x=0})^{1-\alpha}([R]_{x=0})^{\alpha}$$

I_0 is dependent on the concentrations at $x = 0$

Space charge effect (so-called Frumkin effect)

Gouy-chapman case: potential profile

Let's consider the Gouy-Chapman case with +ze/-ze defects:



$$\rho(x) = 2zec_{i,\infty}\sinh(-\frac{ze\phi(x)}{k_BT})$$

Poisson's equation

$$\frac{d^2\phi}{dx^2} = -\frac{\rho(x)}{\varepsilon_0\varepsilon_r} = \frac{2zec_{i,\infty}}{\varepsilon_0\varepsilon_r}\sinh(\frac{ze\phi(x)}{k_BT})$$

$$\frac{d\phi}{dx} = -\frac{2k_BT}{ze\lambda_D}\sinh(\frac{ze\phi(x)}{2k_BT})$$

$$\lambda_D = \sqrt{\frac{\varepsilon_0\varepsilon_r k_BT}{2z_i^2 c_{i,\infty} e^2}}$$

$$\frac{\tanh(ze\phi(x)/4k_BT)}{\tanh(ze\phi_0/4k_BT)} = \exp(-\frac{x}{\lambda_D})$$

$\phi(x)\sim x$
(universal form)

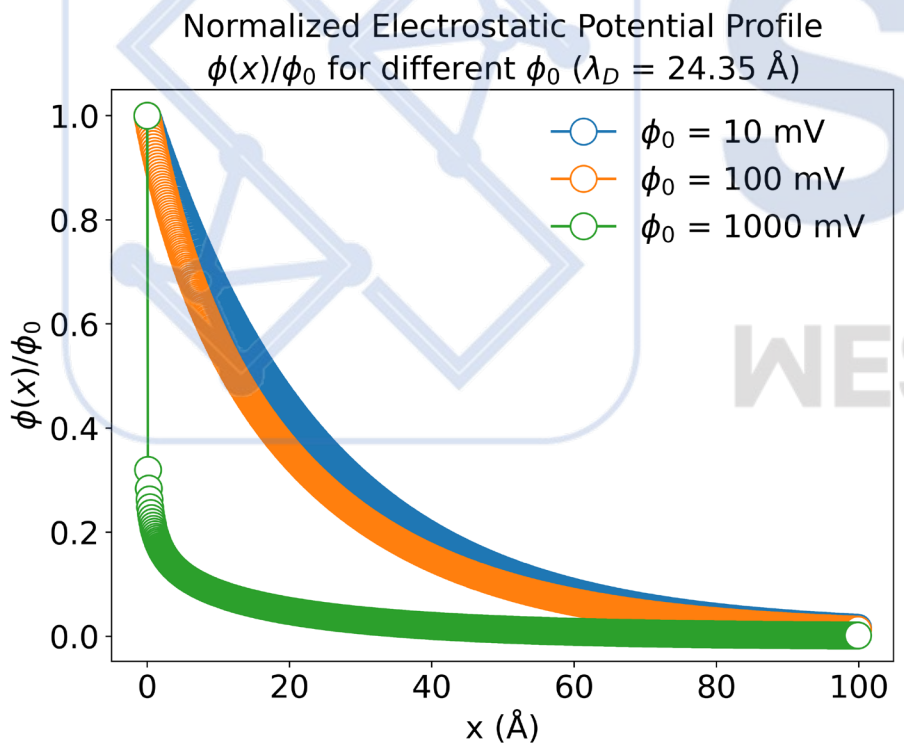
HW 2, Problem 1: Exact Solution for Gouy-Chapman case

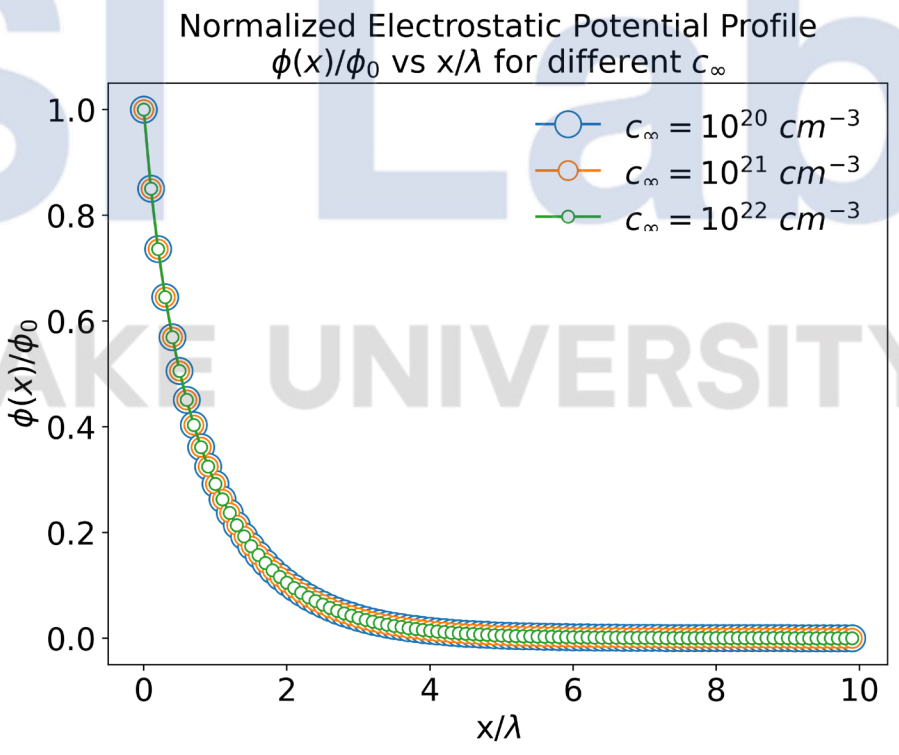
$$\frac{\tanh(ze\phi(x)/4k_BT)}{\tanh(ze\phi_0/4k_BT)} = \exp(-\frac{x}{\lambda_D})$$

$\phi(x) \sim x$ (universal form)

If $ze\phi_0 \ll k_BT$, we can linearize the equation by using $\tanh x \sim x$:

$$\phi(x) = \phi_0 \exp(-x/\lambda_D)$$





Gouy-chapman case: apply Gauss's Law to get Q_{core}

$$\frac{\tanh(ze\phi(x)/4k_BT)}{\tanh(ze\phi_0/4k_BT)} = \exp(-\frac{x}{\lambda_D})$$

$\phi(x) \sim x$ (universal form)

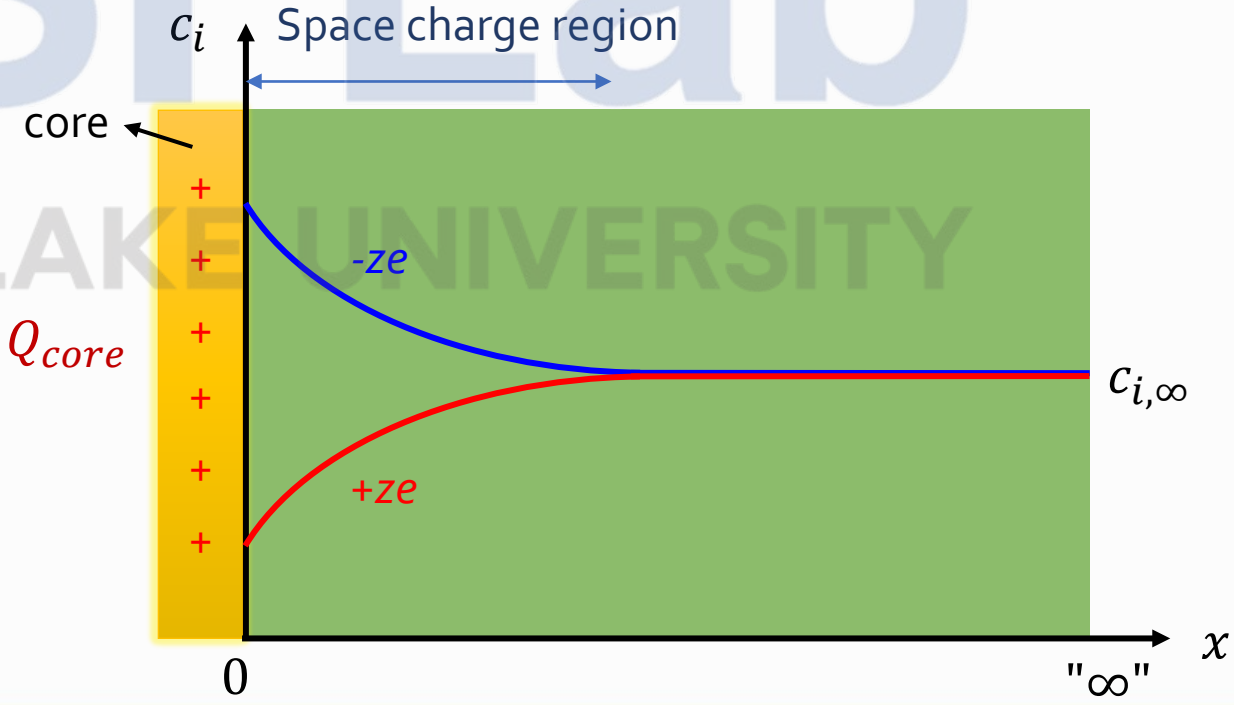
If $ze\phi_0 \ll k_BT$, we can linearize the equation by using $\tanh x \sim x$: → $\phi(x) = \phi_0 \exp(-x/\lambda_D)$

Electric field ← $E = \frac{Q_{enc}}{\varepsilon_0 \varepsilon_r}$ → *"enclosed charge"*

At position $x = 0$:

$$E(0) = -\left.\frac{d\phi}{dx}\right|_{x=0} = \frac{2k_BT}{ze\lambda_D}\sinh(\frac{ze\phi_0}{2k_BT})$$

$$Q_{core} = \varepsilon_0\varepsilon_r \frac{2k_BT}{ze\lambda_D}\sinh\left(\frac{ze\phi_0}{2k_BT}\right)$$



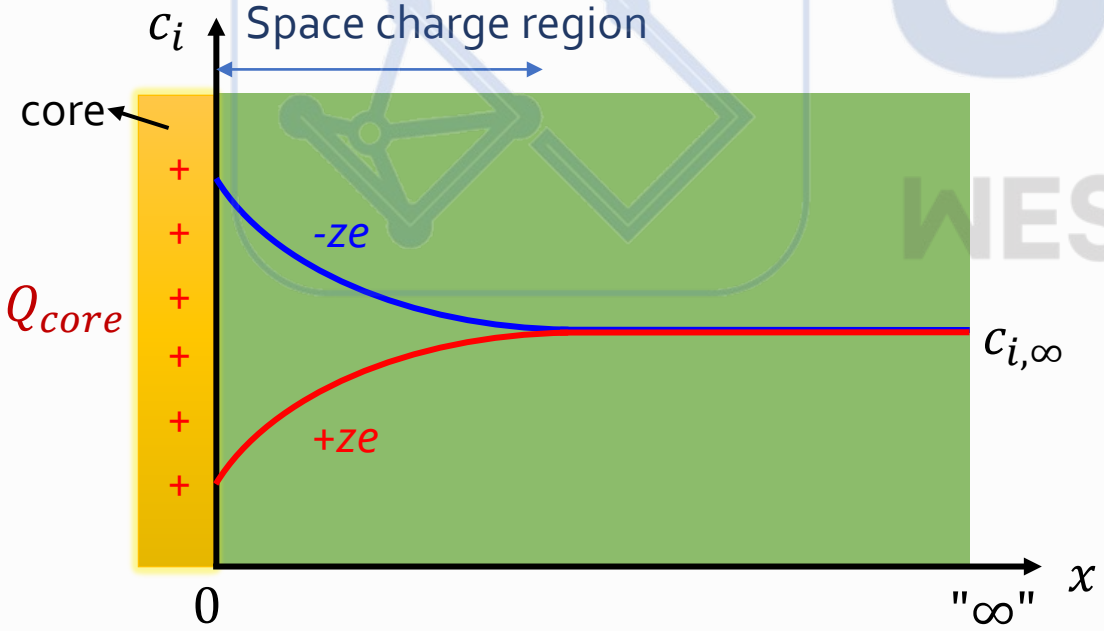
Gouy-chapman case: differential capacitance

We have established the correlation between charge Q_{core} and potential ϕ_0

$$Q_{core} = \varepsilon_0 \varepsilon_r \frac{2k_B T}{ze\lambda_D} \sinh\left(\frac{ze\phi_0}{2k_B T}\right)$$

We can define differential capacitance:

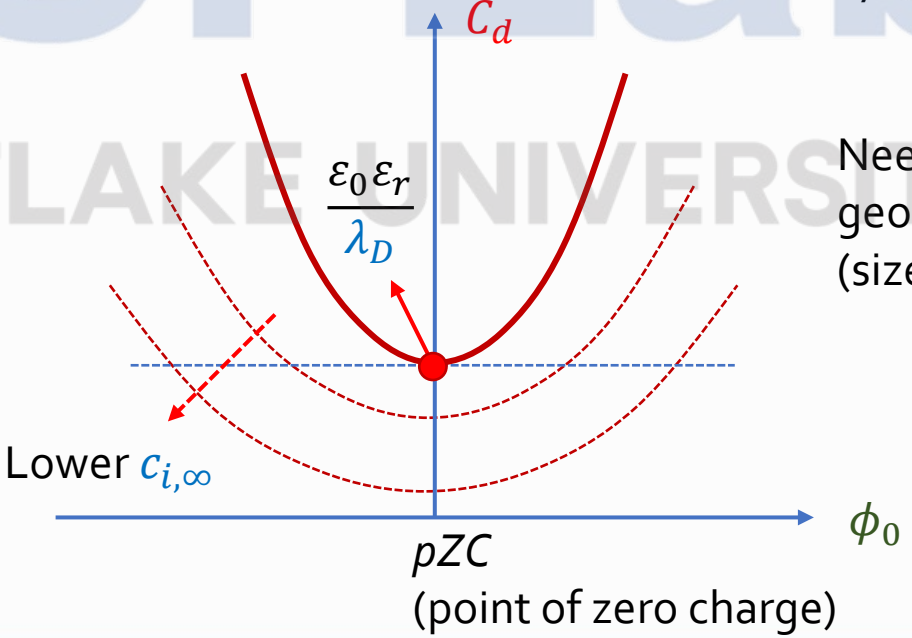
$$C_d = \frac{dQ_{core}}{d\phi_0} = \frac{\varepsilon_0 \varepsilon_r}{\lambda_D} \cosh\left(\frac{ze\phi_0}{2k_B T}\right)$$



Problem:
Capacitance goes to infinite at high potentials

Origin:
Defects are treated as point charges that can be infinitely close to the core.

Need to consider geometry effect (size of defects)



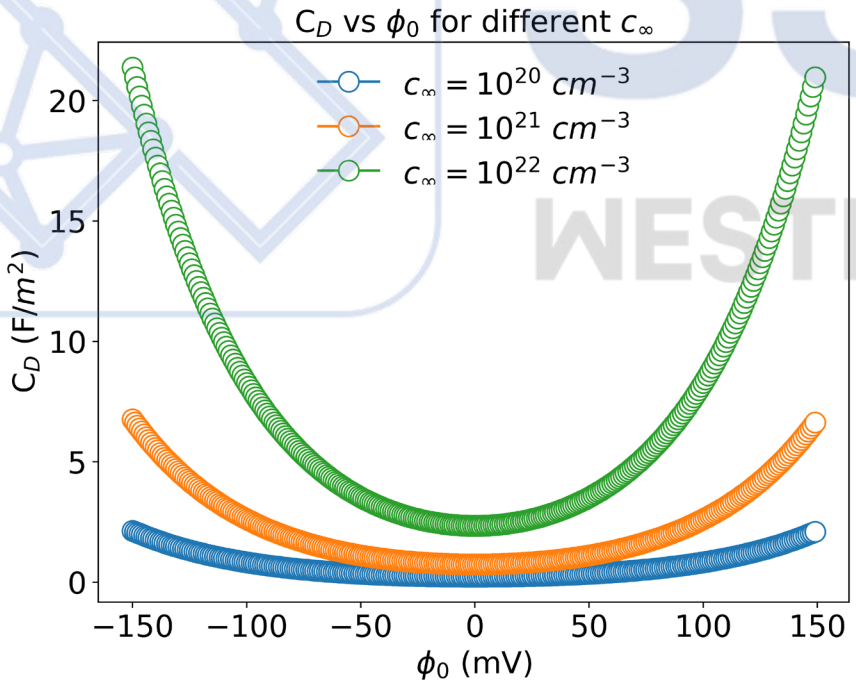
HW 2, Problem 11: Capacitance of Space Charge Layers

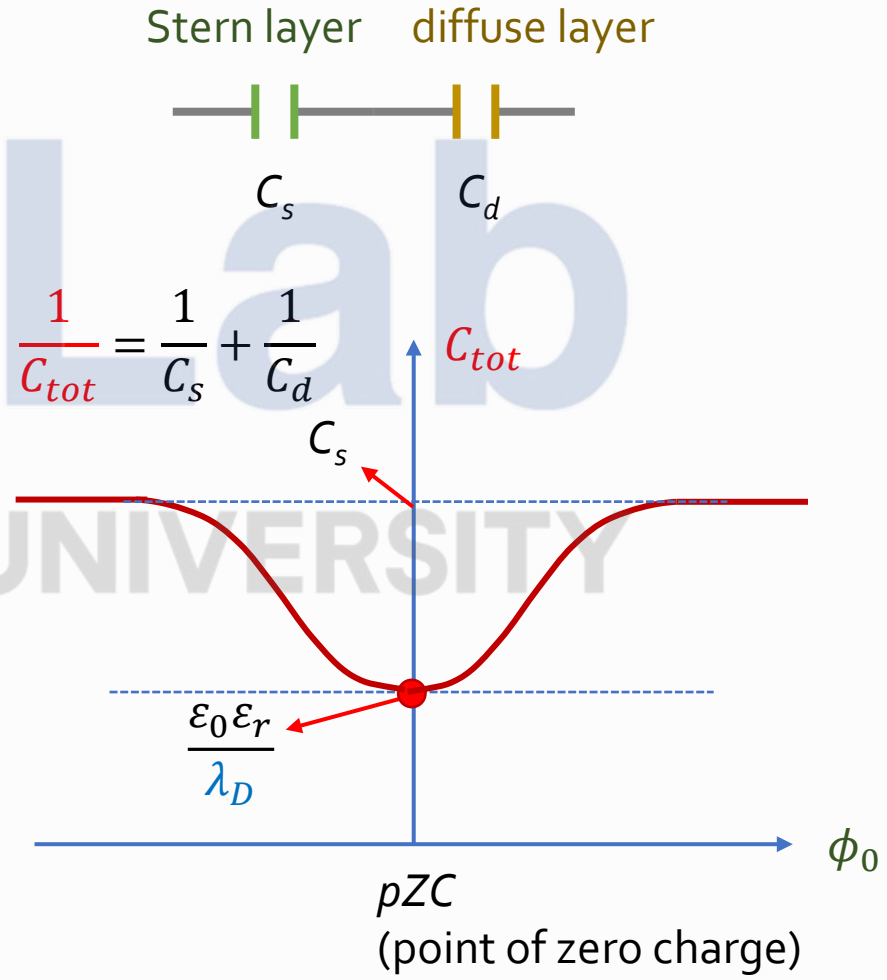
We have established the correlation between charge Q_{core} and potential ϕ_0

$$Q_{core} = \varepsilon_0 \varepsilon_r \frac{2k_B T}{ze\lambda_D} \sinh\left(\frac{ze\phi_0}{2k_B T}\right)$$

We can define differential capacitance:

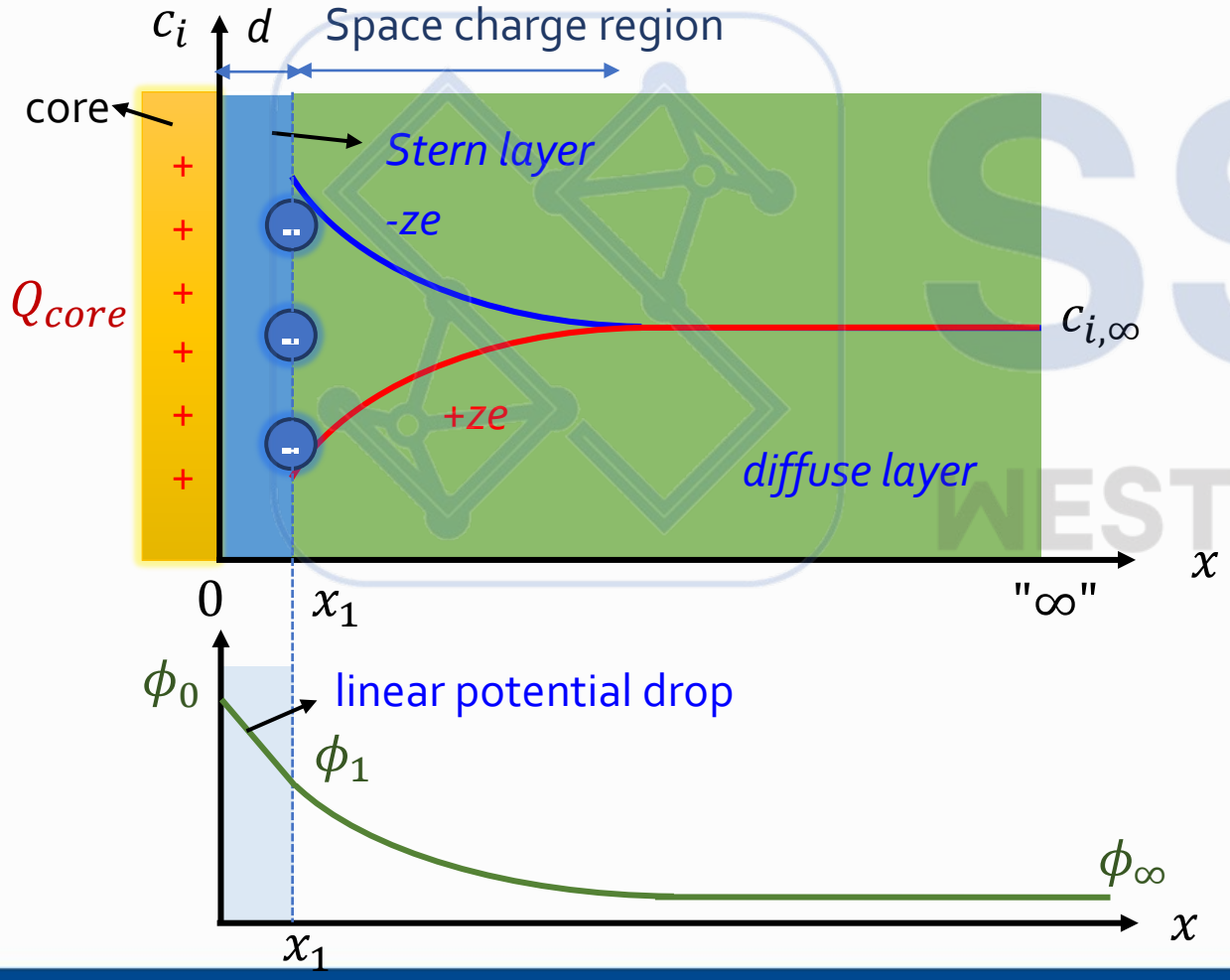
$$C_d = \frac{dQ_{core}}{d\phi_0} = \frac{\varepsilon_0 \varepsilon_r}{\lambda_D} \cosh\left(\frac{ze\phi_0}{2k_B T}\right)$$

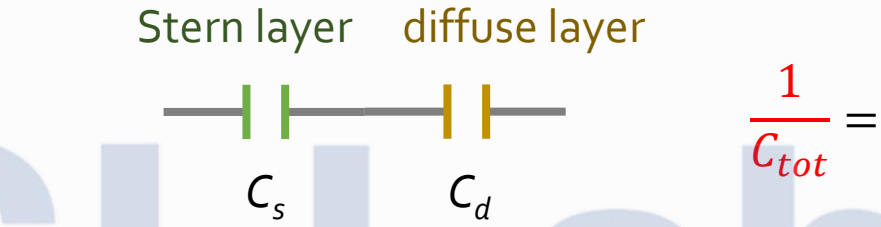




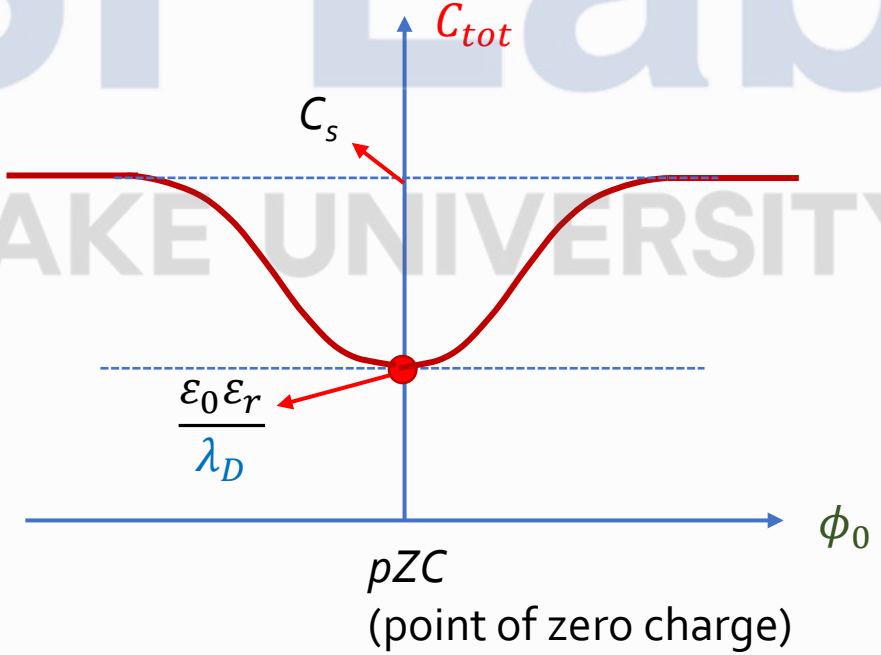
Gouy-chapman case: Stern layer

One must consider the size of defects to solve the capacitance issue:

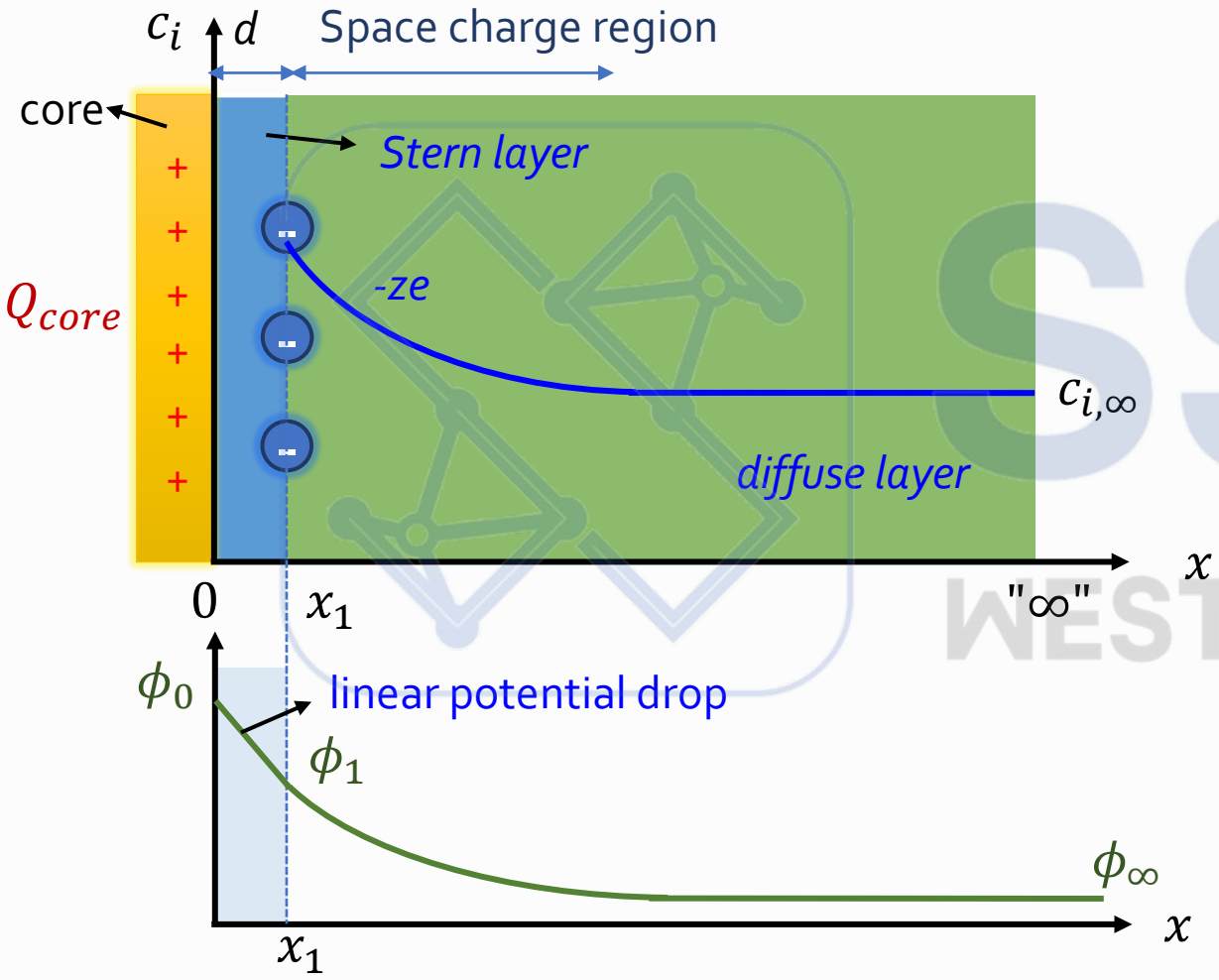




$$\frac{1}{C_{tot}} = \frac{1}{C_s} + \frac{1}{C_d}$$



Frumkin effect: the contribution of Stern and diffuse layers



$$O^{-(z-1)} + e^- \underset{k_a}{\overset{k_c}{\rightleftharpoons}} R^{-z}$$

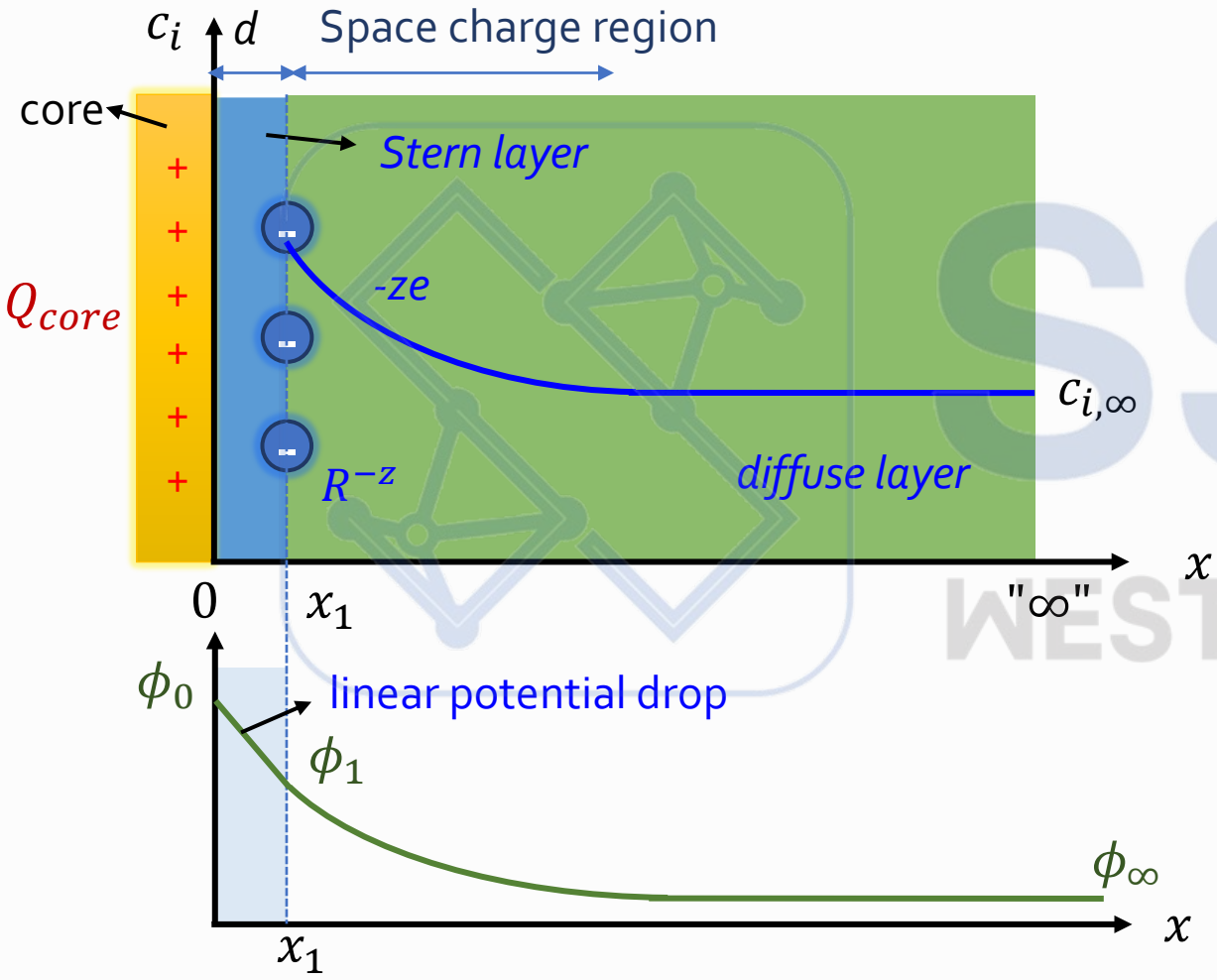
$$I_a = FA\overleftarrow{R} = FAk_a[R]_{x=x_1} = FAk^0 exp\left(\frac{(1-\alpha)F\Delta E}{RT}\right)[R]_{x=x_1}$$

- *Concentration effect*: $[R]_{x=x_1} = [R]_{x=\infty}\exp(zF\phi_1/RT)$

- *Potential effect*:
  w/o Stern layer: $\longrightarrow \Delta E = E - E^{0\prime}$
  w/ Stern layer: $\longrightarrow \Delta E = E - E^{0\prime} - \phi_1$

The *Frumkin effect* is the combination of both effects from the change of concentration and potential!

Frumkin effect: the contribution of Stern and diffuse layers



$$I_a = FA\overleftarrow{R} = FAk_a[R]_{x=x_1} = FAk^0 exp\left(\frac{(1-\alpha)F\Delta E}{RT}\right)[R]_{x=x_1}$$

$$[R]_{x=x_1} = [R]_{x=\infty}\exp(zF\phi_1/RT)$$

$$\Delta E = E - E^{0'} - \phi_1$$

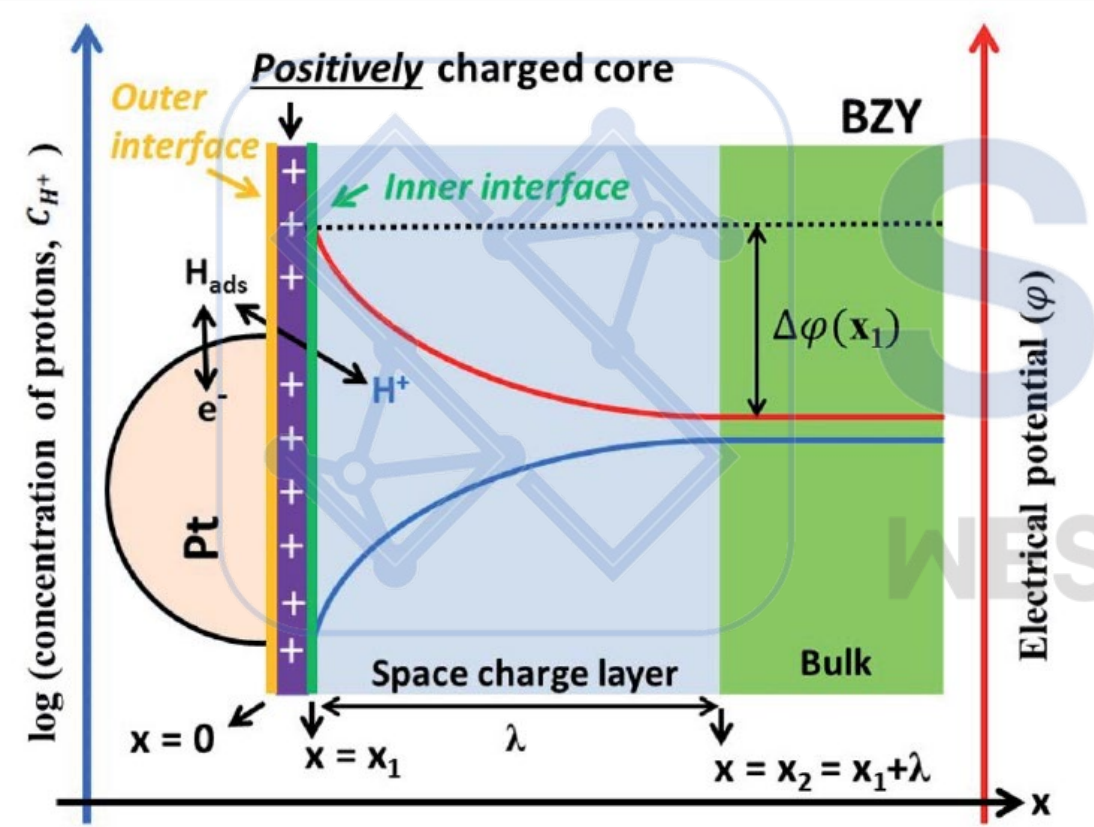
$$I_a = FAk^0 exp\left(\frac{(1-\alpha)F(E-E^{0'}-\phi_1)}{RT}\right)[R]_{x=\infty}\exp(\frac{zF\phi_1}{RT})$$

$$= FAk^0 exp\left(\frac{(1-\alpha)F(E-E^{0'})}{RT}\right)[R]_{x=\infty}$$

$$\exp(\frac{(z-(1-\alpha))F\phi_1}{RT})$$

Modification from *Frumkin effect*

An example: hydrogen oxidation *rxn* (HOR) at Pt/BZY interfaces



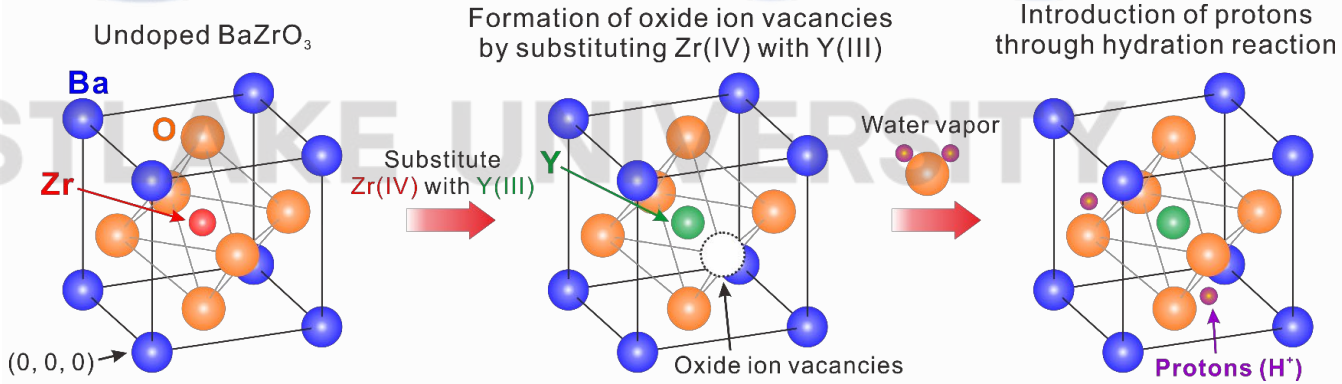
BZY = $BaZr_{0.9}Y_{0.1}O_{3-x}$

$$H_2O + V_O^{\cdot\cdot} + O_O^{\times} \rightleftharpoons 2OH_O^{\cdot}$$

H^+

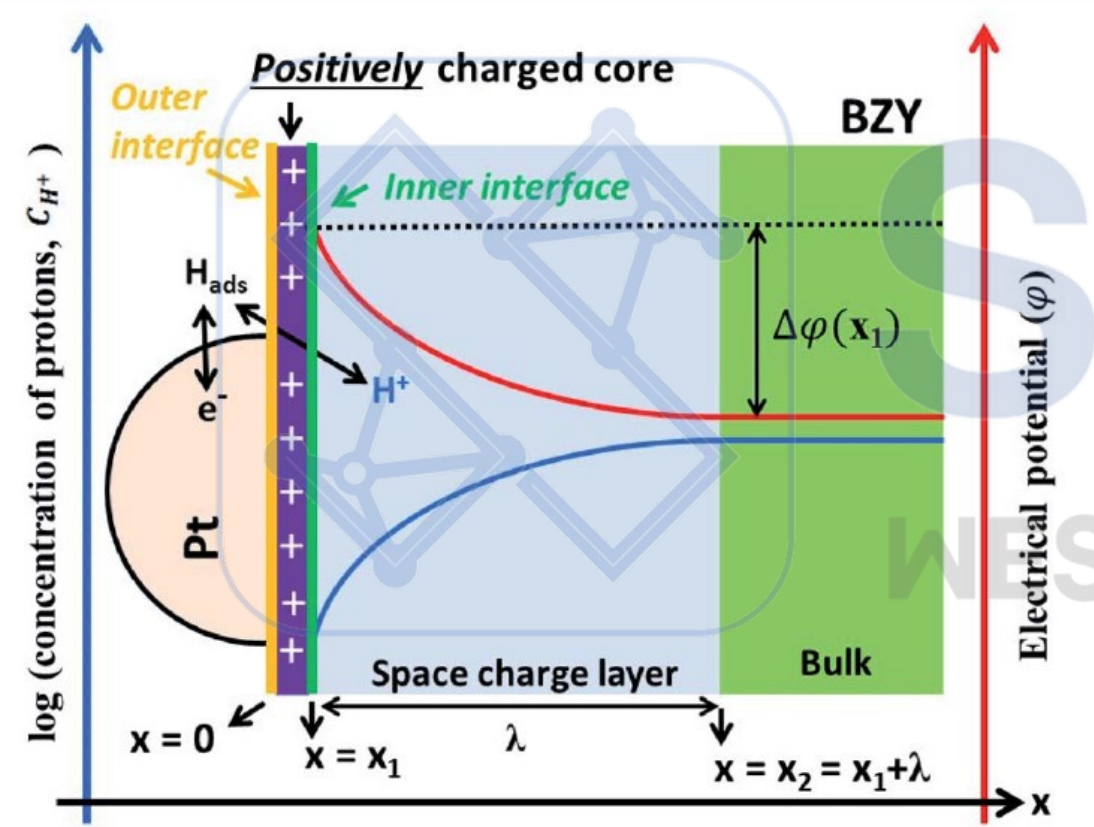
Electrochemical rxn:

$$H_{ads} \rightleftharpoons OH_O^{\cdot} + e'$$



Courtesy of Prof. Donglin Han (Soochow University)

An example: hydrogen oxidation *rxn* (HOR) at Pt/BZY interfaces



BZY = $BaZr_{0.9}Y_{0.1}O_{3-x}$

$$H_2O + V_O^{\cdot\cdot} + O_O^{\times} \rightleftharpoons 2OH_O^{\cdot}$$

H^+

Electrochemical rxn:

$$H_{ads} \rightleftharpoons OH_O^{\cdot} + e'$$

- Due to the positive space charge core, the proton ($OH_O^{\cdot}$) concentration at $x = x_1$ becomes depleted;
- This will lead to a modified exchange current density due to the Frumkin effect.

Exchange current

$$I_0 = FA\,k^0([OH_O^{\cdot}]_{x=x_1})^{1-\alpha}{\theta_H}^{\alpha}$$

modified proton conc. *H surf. coverage*

Review of course content

Defect chemical equilibrium

Brouwer diagram:

[def] ~ lna_i

i = charge neutral species (*e.g.*, O2, Li)

Space charge layers (SCLs)

$$\phi\ (x_1) \neq \phi\ (x_2)$$

$$a_i\ (x_1) \neq a_i\ (x_2)$$

- Gouy-Chapman case
- Mott-Schottky case

"frozen" defects

$$\frac{\partial \tilde{\mu}_i}{\partial x} = 0$$

Solid State Ionics:

Transport and *Reaction* of *Ionic defects*

$$\frac{\partial \tilde{\mu}_i}{\partial x} \neq 0$$

$$\tilde{\mu}_i = \mu_i^0 + RTlna_i + z_iF\phi$$

Ionic defect transport

- Diffusion: $\nabla\mu \neq 0$ ($\nabla c \neq 0$)
- Drift: $\nabla\phi \neq 0$
- Coupled drift-diffusion:

$$J_i = -\frac{\sigma_i}{z^2F^2}\nabla\tilde{\mu}_i$$

Concerted ion-electron transport

Chemical diffusivity:

$$D_O^\delta = \frac{RT}{4F^2}\frac{\sigma_O^\delta}{c_O^\delta}$$

Solid-state electrochemistry

- OCP: $E = (\tilde{\mu}_{e',a} - \tilde{\mu}_{e',c})/\mathrm{F}$
- Kinetics: Butler-Volmer *eqn.* Marcus(-Hush-Chidsey)

Things we have discussed in this lecture

Kinetics of Electrode Reactions:

- How to build a model for charge transfer at electrode surfaces?
- What are the key assumptions for Butler-Volmer equations?
- What does the η-I curve look like at small/large overpotentials?

Frumkin Correction:

- What is the Frumkin Effect? How does the space charge layer affect the kinetics at electrode surfaces/interfaces?

Goal of this lecture: you should be able to answer the questions above now (hopefully) :)

西湖大學
WESTLAKE UNIVERSITY

End of Lecture 10
Solid State Ionics Fall 2023

固态离子学课题组网站

课题组微信公众号